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Further Studies in the Carbonization of North Dakota Lignite

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FURTHER STUDIES IN THE CARBONIZATION OF
NORTH DAKOTA LIGNITE.

1. The Gaseous Products of Low Temperature
Carbonization of Lignite.

2. The Effect of Aluminum Chloride Hydrate
and Pitch on the High Temperature
Carbonization of Pre-Carbonized Lignite.

3. The Effect of Blending with Bituminous Coals
on the High Temperature Carbonization of Lignite.

by

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This Thesis presented by James Roscoe Taylor as a partial fulfillment of the requirements for the degree of Master of Science in the University of North Dakota is hereby approved by the Committee in charge of his work.

Elwin E. Harris

INTRODUCTION.

The coal supply of the United States, although at one time considered inexhaustible, is being used at a rate that will in the course of time result in the depletion of the reserve particularly of bituminous and anthracite coal. In this connection Dr. R. G. Fernald[1], Director, Mechanical Engineering Department, Towne Scientific School, University of Pennsylvania, is responsible for the statement: "In fifteen years, North Dakota lignite, which has a 35-40 per cent moisture content, may be one of our leading fuels". Because of the fact that the low rank fuels constitute the major portion of the coal reserve, foresight on the part of the fuel economist has caused a directing of attention to the better utilization of such fuels as lignite and sub-bituminous coal.

The estimated reserve[2] of lignite in the United States is nine hundred thirty nine billion tons and of sub-bituminous coal nine hundred ninety six billion tons. North Dakota alone has an estimated reserve[2] of six hundred billion tons of lignite or nearly two-thirds of the lignite reserve of the United States.

Lignite is classed as a young coal, of the non-caking type. As mined it contains from 30-40 per cent moisture, approximately 50 per cent of which it loses upon exposure to air. During the drying process slacking occurs which causes a disintegration and consequent loss of form value. The heat value ranges from 6,000 to 7,000 B. t. u. per pound as mined. The property of slacking, the high moisture content on which freight must be paid and the low heat value limit the radius to which lignite can be shipped with profit.

Research is being carried on in the School of Mines of the University of North Dakota with the purpose of developing from this low grade coal a fuel with a higher heat value, one which does not slack on exposure to weather, and one which can compete on the open market with the higher grade eastern fuels. Although lignite is ordinarily considered of the non-coking type, carbonization offers a possible solution to the problem. The problem is to obtain a coherent residue of coke of relatively high heat value that will withstand handling and weathering and also to obtain a commercial gas.

High temperature carbonization of raw lignite yields a soft powdered char that possesses none of the properties of coke. The tar yields are low and the resulting gas contains from 15 to 20 per cent carbon dioxide. In contrast, the high temperature carbonization of coking coals yields a firm resistant coke, higher yields of tar, and a gas that is low in carbon dioxide.

Gauger and Salley[3] studied the effect of the addition of various inorganic materials on the coking properties of North Dakota lignite. They found that "hydrates of aluminum chloride, sulfate and nitrate, magnesium sulfate and chloride, and strontium chloride alter the structure of the char produced yielding a hard pseudo-coke differing materially from the soft powdered char of the untreated coal, whereas the anhydrous salts produced soft fine chars." Of the materials tested hydrated aluminum chloride gave the hardest pseudo-coke. Although not stated in their published article Gauger and Salley also found that the carbonization of raw lignite with aluminum chloride gave a gas similar in composition to

that from the carbonization of raw lignite alone. This indicated that the high oxygen content of the coal was driven off during the carbonization process as carbon dioxide before the temperature was raised high enough to result in the formation of carbon monoxide.

Pre-carbonization at low temperature followed by subsequent carbonization with aluminum chloride at high temperatures offered a possible solution to the problem of the elimination of the high carbon dioxide content of the gas and, at the same time, the production of a coherent char or coke.

Part 1 of this work includes a study of the gaseous distillation products in order to determine the temperature at which an appreciable quantity of carbon dioxide is evolved and also to determine the temperature at which hydrogen, carbon monoxide, and methane was evolved. The work was started on the assumption that at some temperature a large amount of the oxygen might be driven off as carbon dioxide with the minimum loss of hydrogen, carbon monoxide and methane. This assumption was based on the following reasoning: A study of critical oxidation temperatures of lignite by Gauger and Brady[4] showed that, in the absence of oxygen, carbon dioxide began to come off from lignite coal as low as 100° C. and that at higher temperatures considerable quantities were evolved. This evolution of carbon dioxide takes place considerably below the temperature at which the carbon dioxide begins to be acted upon by carbon in the reaction $CO_2 + C \rightleftharpoons 2CO$. Furthermore, the hydrogen and methane in the gas is produced by the cracking of the organic compounds contained in the coal. This cracking does not take place in carbonization until temperatures of approximately

500° C. are reached.

Part 2 of this work is a continuation of the study of the catalytic effect of aluminum chloride hydrate on the coking properties and gaseous products of high temperature carbonization of lignite; using, rather than the raw lignite, the lignite which has been pre-carbonized in accordance with the data in part one. Because of the removal of the tars in the pre-carbonization process, pitch was added to form the coking binder.

Part 3 consists of a study of the effect of blending bituminous coals with lignite char on the nature of the coke and gas produced by carbonization at 850° C.

Percy[5] showed that the heating of a non-coking coal with a coking coal gave a firm and resisting coke. Roberts[6] states that lignite distilled at any desired temperature up to 1,000° C. in the absence of air could be pulverized and used as an inert material for blending with coking coal in suitable proportions. Lander and McKay[7] refer to the blending of a caking with a non-caking coal and in some of the work represented by them the proportion of non-coking to coking is as high as 70:30.

The mechanism of blending is not very well understood but it appears that the coking coal forms a plastic layer and that the coal becomes semi-liquid. This semi-liquid mass of the coking coal surrounds the non-coking particles and on subsequent carbonization the plastic layer cokes and holds the non-coking coal firmly. On first appearance it would seem that the blending process is relatively simple but the question as to whether or not the coking coal in the fluid state has the property of

wetting the non-coking coal, e.g. the question of miscibility, enters.

The problem is to find a bituminous coal of the coking type that has the property of wetting the lignite char and one which has enough excess binder to give a firm and resistant coke upon the subsequent carbonization.

Part three of this work gives the results of the blending of six different bituminous coals with lignite char, both in the presence and absence of aluminum chloride hydrate, under a definite set of conditions.

Part 1.

The Gaseous Products of Low Temperature Carbonization of Lignite .

Experimental

Materials:

The lignite used in all the experiments was taken from the Kincaid mine at Kincaid, North Dakota. This coal is fairly representative of North Dakota lignites, although the sample used was a little lower in ash than that from most of the other mines in the state. A large sample of this coal was allowed to air dry and then ground to pass through a 14 mesh screen and sealed in Mason jars.

Apparatus:

The complete equipment for carbonizing is illustrated in figure 1. The retort A was of aluminum of the same type as used by Franz Fischer in his research on German coals[8]. The retort was heated by three Fischer type burners. A platinum platinum-rhodium thermocouple was used for measurement of temperature. Condenser B was fastened to the retort by a steel union C. The condenser was a glass tube eight inches long and two inches in diameter sealed at one end. It was cooled by running water. The outlet from the condenser was connected to a glass wool filter D. to remove suspended tars. This was connected to a continuous mercury sampling device E which consisted of a T tube with a smaller inside tube which contained a capillary opening into the gas stream. The sampler was connected to a 250 cc. aspirator bottle

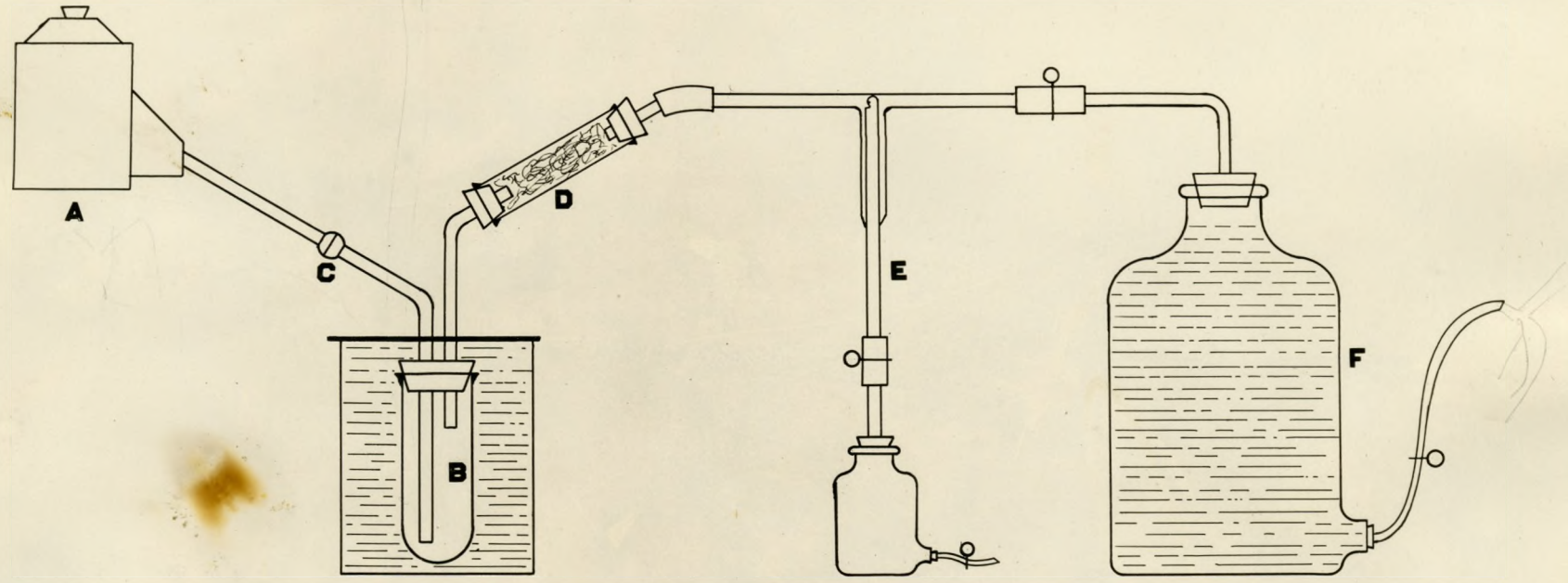

FIG. 1

EXPERIMENTAL APPARATUS
FOR CARBONIZATION OF LIGNITE

filled with mercury. From the T tube the train connected with a large calibrated aspirator bottle G which served as a gas holder.

Procedure:

The procedure used in all of the work, was the same as that used by Gauger and Salley (loc. cit). The proper amounts of the materials were mixed intimately and the resulting mixture briquetted in a small foot cupel machine. The purpose of making the briquets was to prevent any fine lignite dust from being blown out through the offtake pipe during heating. An amount of water was added so that the coal was sufficiently wet to cause adherence, but not wet enough to allow any water to squeeze out during the briquetting process.

The briquets were placed in the retort as rapidly as possible and the rest of the train connected. The retort was heated to the desired temperature in from twelve to fifteen minutes and held at that temperature for one hour. After cooling, the weight of the briquet and the volume of gas were recorded. No attempt was made to recover the condensed tar because of the lack of an accurate method of separation of tars from the water.

The gas was analyzed by means of a standard modified Orsat of the Bureau of Mines type. Proximate analyses of representative chars were made.

Results and Discussion

Tables Nos. 1, 2 and 3 give the results of this series of experiments.

Table 1

Temp. of Distill.	Vol. of Gas per 100 G. dry coal	Per cent analysis CO_2	Ill.	H_2	CO	CH_4	C_2H_6	
400°	4,970	62.4	1.8	1.9	7.9	8.3	2.0	84
450°	7,850 (2880)	61.2	2.8	5.7	11.1	9.4	4.8	95.
500°	12,400 (4550)	50.2	3.0	14.5	7.0	19.5	2.1	96.3
550°	16,200 (3800)	42.9	2.1	27.1	9.2	20.1	1.1	102

Table 2

Temp. of Distill.	C. C. of gas per hundred grams of dry lignite CO_2	Ill.	H_2	CO	CH_4	C_2H_6	G of Char per 100 G dry coal
400°	3,100 (1700)	86	92	384	403	97	80.7
450°	4,800 (1400)	216	445	865?	730	378	77.8
500°	6,200 (750)	332	1,600	780	2,160	221	72.5
550°	6,950	338	4,420	1,480	3,350	160	70.0

25 Char at 450

In order to compare the gas yields the curves in figure 2 were plotted.

A study of the curves shows that a large amount of the oxygen in lignite can be eliminated as carbon dioxide by pre-carbonization before there is an appreciable evolution of hydrogen and methane. The temperature to which lignite should be pre-carbonized was determined by the highest ratio by volume of carbon dioxide to hydrogen. This temperature was 450° C.

Table 3 gives the analysis of the original coal and the char (450°) on the dry basis.

Table 3.

	Volatile Matter	Fixed Carbon	Ash	B. t. u.
Original lignite	45.30	47.90	6.80	11,040
450° Char	19.91	67.67	12.42	12,110

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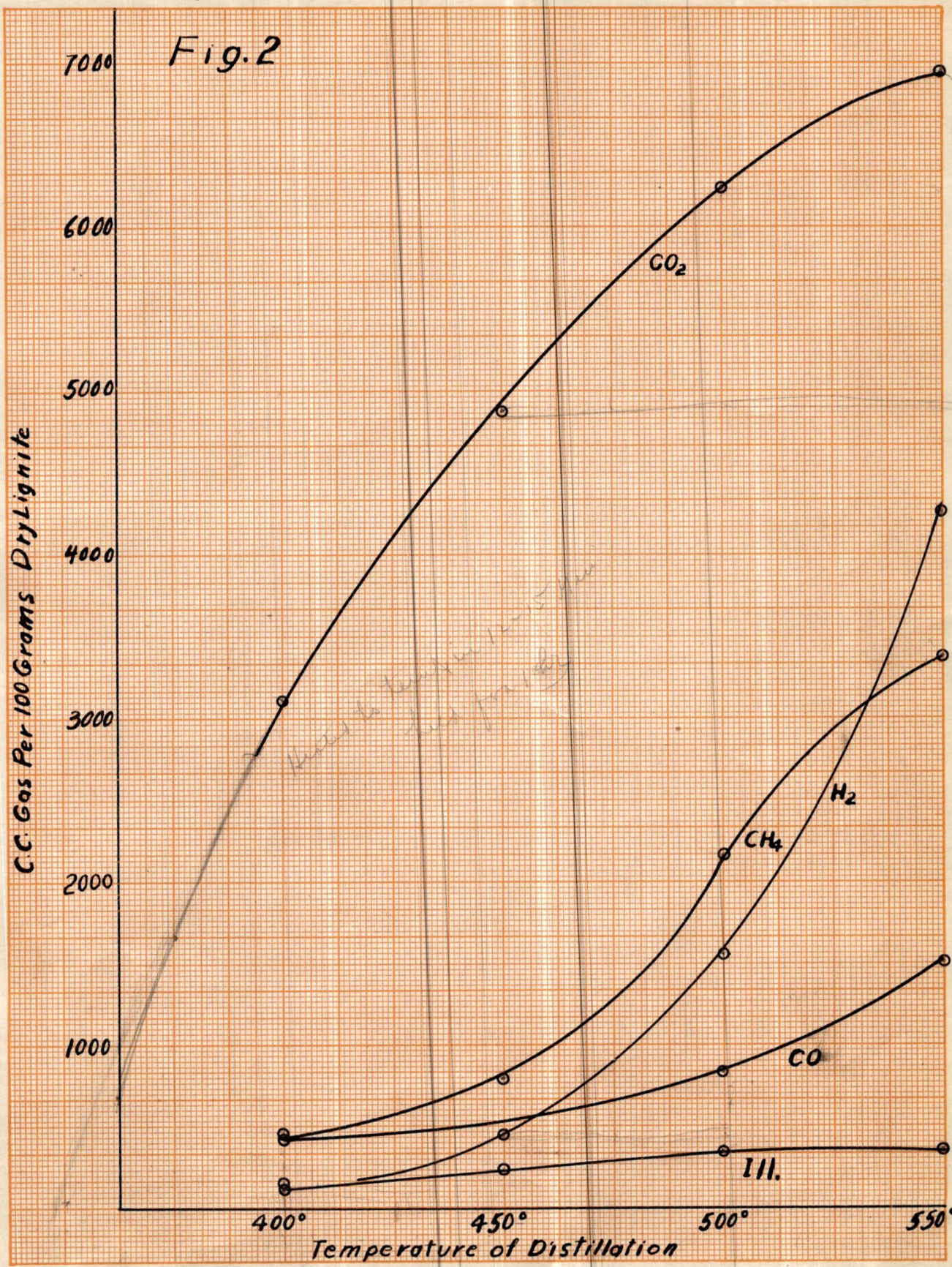
Fig. 2



Part 2.

The Effect of Aluminum Chloride Hydrate and Pitch on the High Temperature Carbonization of Pre-Carbonized Lignite.

Materials:

The coal used was from the Kincaid mind, Kincaid, North Dakota. This coal was crushed to 1/4 inch size and pre-carbonized for one hour at 450° C. in accordance with the data found in part one. After carbonizing the sample was ground to pass a 14 mesh screen and sealed in mason jars.. The pitch used was a petroleum residue from the Skelly Petroleum Company, El Dorado, Kansas. This pitch or, as it is called by W. F. Rittman[9] of Carnegie Institute of Technology, "Bituminous Coal from Petroleum", is the product of cracking refuse oil in a continuous still. When hot it can be pumped in fluid condition but on cooling it hardens into a friable mass that resembles bituminous coal in analysis. The composition of this pitch is, volatile matter, 45%, fixed carbon, 51%, ash 4% and B.t.u., 15,600. The pitch was ground to pass a 100 mesh screen and bottled in a mason jar.

Effect of grinding

Apparatus:

The apparatus used was the same as in part one except that a nichrome retort with a screw cap was substituted for the aluminum retort in figure 1 A. Nichrome metal was used because it does not warp appreciably at high temperature and because it exerts little or no catalytic effect on the carbonizing of the coal. The only other modification in the apparatus was the placing of a manometer between the glass wool filter D and the sampling tube E. This was

done because it was impossible to keep the retort air tight at high temperatures. In order to assure a minimum leakage without the danger of drawing air into the train during the process the pressure within the train was kept at from one to three mm. mercury.

Procedure:

The procedure was the same as that in the preceding part with the exception of the rate of heating. The retort was heated by blast lamps in a furnace made of fire brick. The rate of heating was such that the temperature of the retort was raised to 850° C. in one hour and held at that temperature for thirty more minutes.

Data and Discussion.

Before starting this series several preliminary experiments were run to determine the effect of different types of pitches on the coking of the lignite char on the assumption that it would be possible to find a pitch that would be miscible with the lignite char and this act as a medium for cementing the particles of lignite char together. In the case of bituminous and asphalt pitch a microscopic study of the resulting chars after carbonization showed that the pitch was coked in small ellipsoidal particles and that there were no signs of miscibility of the pitch and the lignite char. However, in the case of the Skelly pitch there was definite evidence of some miscibility between the coked pitch and the lignite char.

This served as a basis for this series of experiments. A second series of preliminary experiments was run in order to determine the proper amount of Skelly pitch to add to the lignite char. The mixtures used were: 25 g. of lignite char (450°C.) 1.25 g.

$AlCl_3 6H_2O$ with a varying amount of pitch. The results of this series showed that 3.00 grams of pitch to each 25 g. of char gave the best results. Amounts below that gave inferior cementing of the particles and amounts above seemed to have no added effect on the hardness of the resulting char or pseudo-coke.

Table 4 gives the results of varying the amount of $AlCl_3 6H_2O$ on the carbonization of pre-carbonized lignite.

In order to compare the char yields the aluminum chloride hydrate was assumed to be converted to the oxide (Al_2O_3) and then the following formula was used:

$$\text{Grams char less compound formed per 100 grams lignite} = 100 \times \frac{\text{Wt. of char - wt. of compound formed}}{\text{Wt. of lignite taken}}$$

For a discussion of the merits of this assumption see paper by Gauger and Salley. (loc. cit. page 318).

Table 4

Composition of Mix	Wt. of char less compound formed per 100 g. dry lignite ± 0.3 G.	Total Volume of gas cc.per 100 g. dry lignite	C.C. of Gas per hundred grams dry lignite				
			CO_2	Ill.	H_2	CO	CH_4
(1) 25 G char	61.5	22,310	1107	105	13,600	4,000	2,265
(2) 25 G char 3.00 G pitch	63.6	26,800	1190	140	16,420	3,620	2,503
(3) 25 G char 3.00 G pitch 0.25 G $AlCl_3 \cdot 6H_2O$	64.2	30,300	1470	130	16,650	4,110	2,495
(4) 25 G char 3.00 G pitch 0.75 G $AlCl_3 \cdot 6H_2O$	63.7	24,500	790	140	16,900	3,260	2,200
(5) 25 G char 3.00 G pitch 1.25 G $AlCl_3 \cdot 6H_2O$	63.2	24,300	1030	140	16,750	3,020	2,547
(6) 25 G char 3.00 G pitch 1.75 G $AlCl_3 \cdot 6H_2O$	62.9	23,300	1,200	180	15,100	3,040	2,310

Table 5 gives the analysis of the gas from mixes Nos. 1, 2 and 5.

Table 5

Mix No.	Per cent gas analysis CO_2	Ill.	H_2	CO	CH_4	Inert
1	4.8	0.4	59.1	17.2	9.8	8.1
2	4.4	0.5	61.1	13.3	9.3	17.2
5	4.4	0.5	66.7	12.5	10.3	5.6

Table 6 gives the proximate analysis of the chars resulting from mixes Nos. 1, 2 and 5.

Table 6

Mix No.	Volatile Matter	Fixed Carbon	Ash	B. t. u.
1	5.14	82.52	12.34 5.14	12,580
2	4.47	83.87	11.66	12,680
3	2.33	80.2	17.47	11,900

Figure 3 shows the chars resulting from this series.

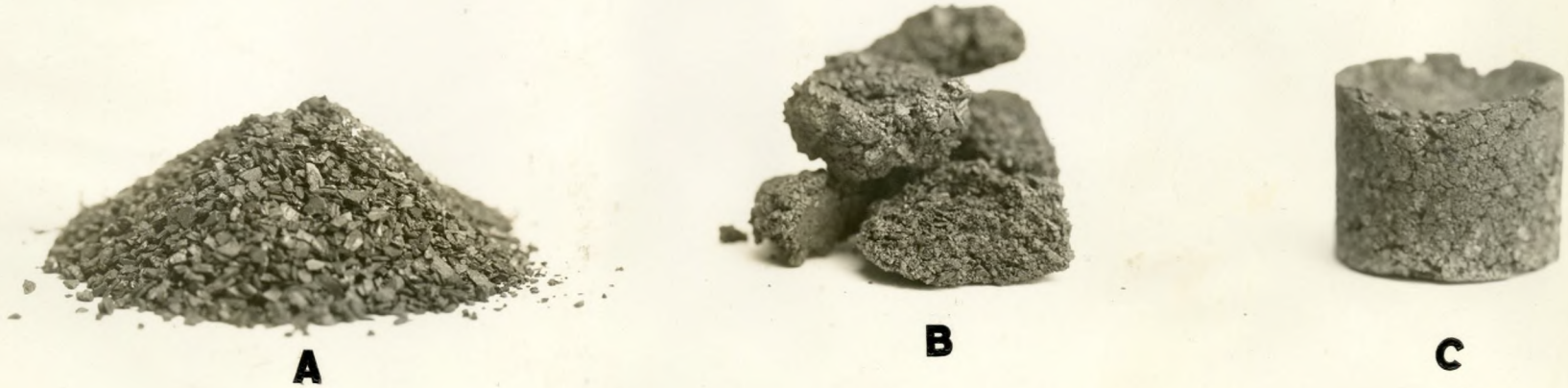
(A) Lignite char (Mix 1)

(B) Lignite char + Skelly pitch (Mix 2)

(C) Lignite char, Skelly pitch and 1.25 grams $AlCl_3 6H_2O$ (Mix 5).

Examination of the photographs reveals very clearly the effect of both the pitch and the aluminum chloride on the character of the resulting char.

An analysis of the gas data is difficult because of the inaccuracy incurred by the inability to make the retort air tight. However, the addition of pitch does increase the hydrogen content which might be expected. As closely as can be determined from the data the aluminum chloride has no effect on the gaseous products. The aluminum chloride does have a decided effect on the character of the char. Up to mix No. 5 each addition of aluminum chloride causes a firmer, denser pseudo-coke. Above that quantity - represented by mix No. 5 - the effect is slight and each increase has less effect.



A B C

FIG. 3

Part 3

The Effect of Blending with Bituminous Coal on the High Temperature Carbonization of Lignite.

Experimental.

Materials:

The lignite used was the same as in part 2 e.g. Kincaid lignite pre-carbonized to 450° C.

The coals used for blending were:

1. Illinois Bituminous (Parr's coal).
2. Red Diamond.
3. Blue Diamond.
4. Gold Edge.
5. Wheelwright lump.
6. Pocahontas.

The bituminous coals were pulverized to pass through 100 mesh.

Procedure:

The procedure was the same as that used in part 2.

Results and Discussion

In order to obtain comparable results the six mixtures used in blending were made up of the same proportions. Fifteen grams of lignite char, 10 grams of the bituminous coal and 8 grams of water composed the mix of the first series.

The resulting chars, or cokes are shown in figure 4, as follows:

A. Illinois Bituminous
B. Red Diamond
C. Blue Diamond
D. Gold Edge
E. Wheelwright lump
F. Pocahontas.

Illinois bituminous gives a very friable, soft coke with very little cementation of the lignite and the bituminous. Red Diamond, Blue Diamond and Gold Edge all gave practically the same structure.

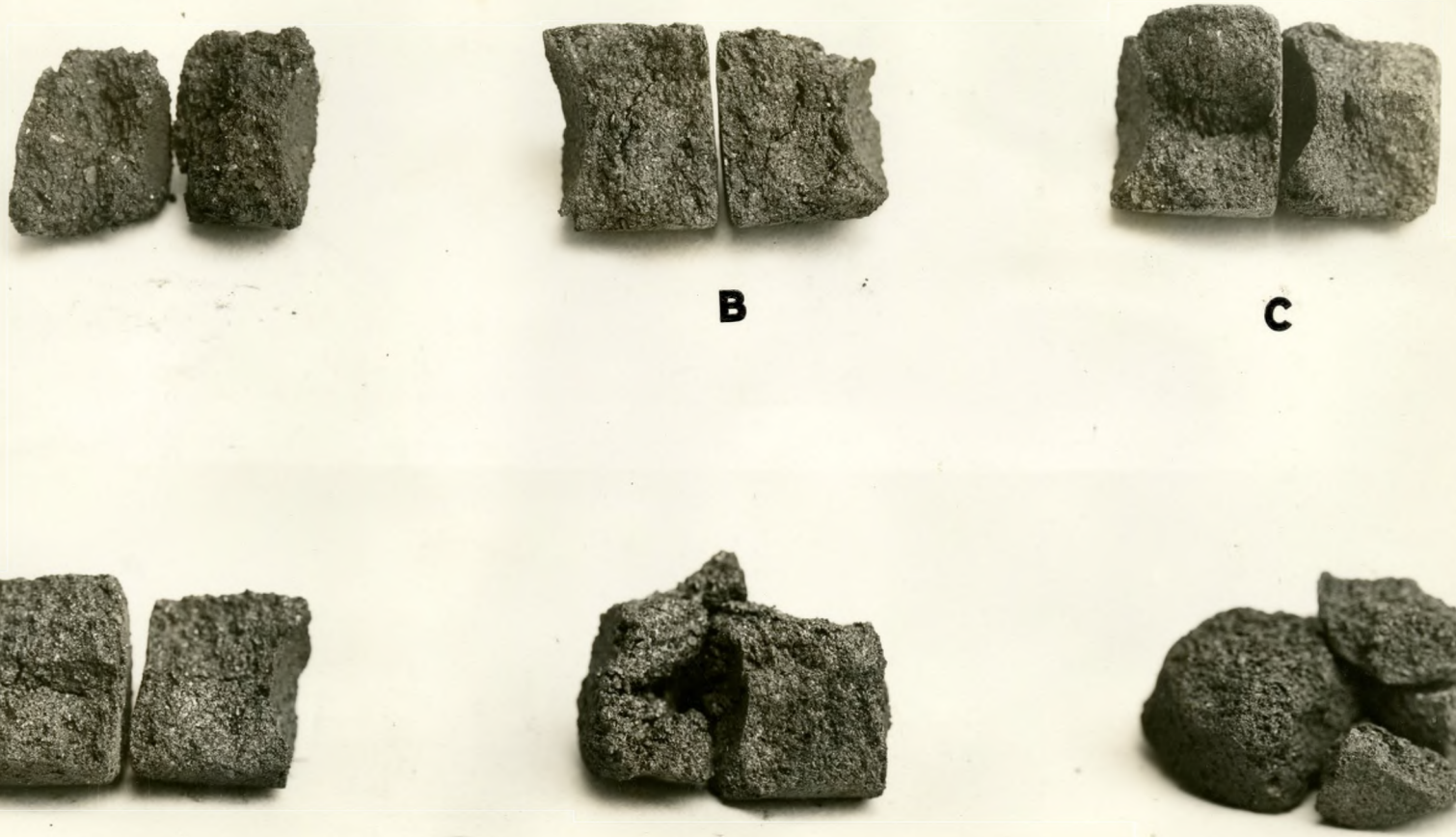


FIG. 4

All were hard, lustrous, of relatively dense structure, and gave the characteristic metallic ring. However, the porous structure of true coke was not very pronounced. Wheelwright coal showed considerable evidence of coking and was accompanied with a slight swelling. The blend with Pocahontas gave a true coke structure. The resulting coke showed considerable swelling, and the porous structure of coke was very pronounced. A microscopic examination seems to indicate that the blending was complete and that the coal and char are completely miscible. Figure 4 in which the cokes have been broken open to show the interior structure illustrates the difference in the blending properties of each coal.

In order to determine the effect of aluminum chloride hydrate on the carbonization and subsequent coking of the different blends a second series was made with the following mix: 15 grams lignite char, 10 grams of the coal to be blended, 1.25 grams of $AlCl_3 6H_2O$ and 8 grams of water. The chars from this series are shown in figure 5, as follows:

A. Illinois Bituminous
B. Red Diamond
C. Blue Diamond
D. Gold Edge
E. Pocahontas

The cokes resulting from the blend plus aluminum chloride hydrate are all of a harder, denser structure than the blends alone. This is particularly noticeable in the case of the Pocahontas-lignite blend. Figure 4 F shows the Pocahontas-lignite blend without the aluminum chloride and figure 5 E shows the Pocahontas-lignite blend with the aluminum chloride. The difference is very pronounced.

A

B

C

D

E

FIG. 5

The apparent complete blending of the Pocahontas and lignite gave a coke structure that was worthy of further study. A series was run varying the amount of Pocahontas in the blend in order to determine how little Pocahontas could be added and still have the characteristic coking. The mixes used were:

	Lignite char	Pocahontas	Water
A	15	10	8
B	16	9	8
C	17	8	8
D	18	7	8
E	19	6	8
F	20	5	8

Figure 6 shows photomicrographs of the resulting chars. The letters below the photographs correspond to the letters above showing the mixes. All were magnified approximately 15 diameters. A, B, and C all showed considerable evidence of swelling and gave a good hard coke structure. D, E and F showed no evidence of swelling and though blending was evidenced there was apparently not enough binder to make the characteristic hard porous coke structure. Mix C, which has the ratio of non-coking to coking of 68:32 compares very favorably with the 70:30 ratio as found by Lander and McKay (loc. cit).

Table 7 gives the analysis of the gas from the carbonization of three of the above blends.

Table 7

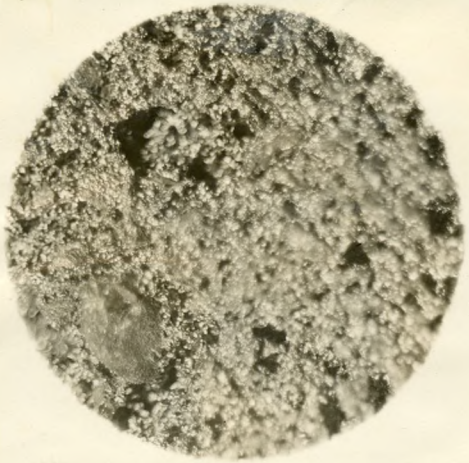
Blend	Gas Analysis in Percent CO_2	Ill.	O_2	H_2	CO	CH_4	Volume of Gas per 100 Grams Blended Coal in C.C.	Calculated B. t. u. per cu.ft.
A	2.3	0.5	2.0	72.3	11.9	11.2	33,300	409
E	2.1	0.8	1.5	67.8	14.0	13.1	33,200	409
F	2.8	0.3	0.5	62.2	13.3	11.8	32,800	370

Although the data in the above table cannot be taken as quantitatively exact because of leakage in the retort, the results are in close enough agreement to indicate that the carbonization of lignite char with Pocahontas coal gives a gas of high enough heat value to be easily carburetted to the standards set for city gas. The carbon dioxide content is worthy of particular note. The carbon dioxide content of the gas from high temperature carbonization of raw lignite is from 15 to 20 per cent. By pre-carbonization of the lignite this has been reduced so that the gas from the blending of lignite and bituminous is as low as 2.0 to 3.0 per cent.. This reduction greatly increases the heat value of the resulting gas and reduces the inactive content of the gas.

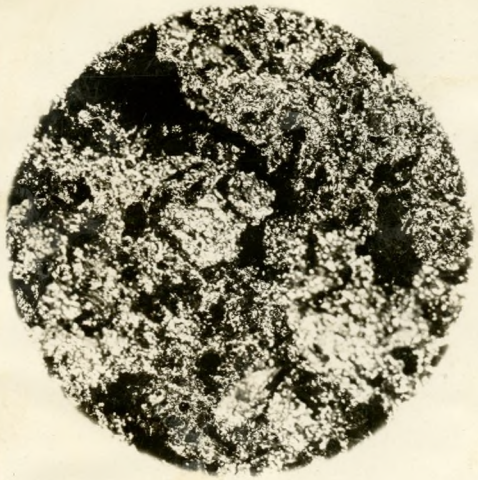
The following table is a proximate analysis of the coke resulting from Blend A.

	Volatile Matter	Fixed Carbon	Ash	B.t.u.
Blend A	3.16	86.01	10.82	13,060

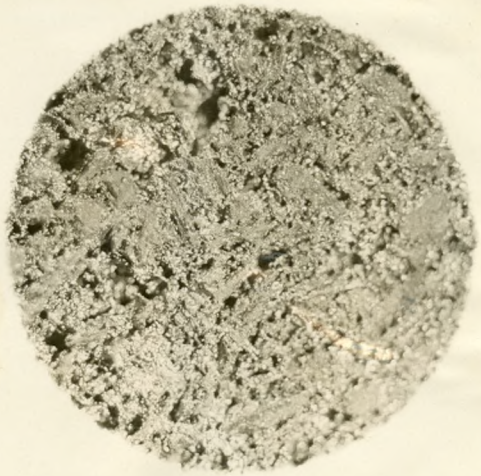
In conclusion it may be said that this work on blending is a bare introduction to the field. Other coals than the ones studied in this work may have possibilities. There is also a large field for study in the blending of Pocahontas with lignite. The effect of particle size, rate of heating, effect of pressure and the effect of metallic catalysts are separate phases worthy of further study.



A

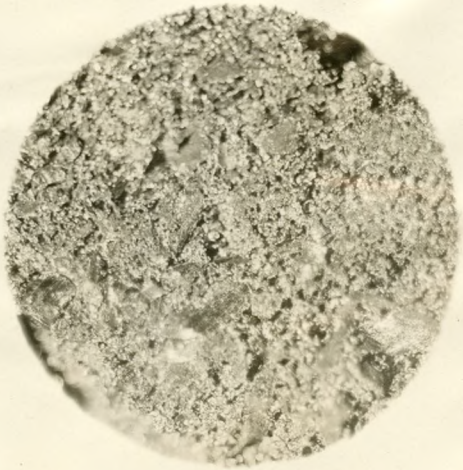


C



D

F



E

FIG 6

Conclusions.

1. Pre-carbonization offers a solution to the problem of elimination of the high oxygen content of lignite coal with consequent improvement of the gas quality.

2. Carbonization of pre-carbonized lignite with the aid of aluminum chloride hydrate as a catalyst and pitch gives a gas of relatively high heat value but the resulting char or pseudo coke is not of sufficient strength to warrant the adaptation of this type of carbonization to commercial practice.

3. The field of blending offers possibilities for the solution of the problem of coking lignite coal.

4. A good coke and a relatively high heat value gas can be obtained from the high temperature carbonization of pre-carbonized lignite with Pocahontas coal.

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